Chromic acid is one of the most versatile of the available oxidising agents, reacting with almost all types of oxidisable groups. The reactions often may be controlled to yield largely one product and this makes chromic acid oxidation a useful synthetic tool. As a result of the pioneering work of Westheimer and his collaborators and of the many investigations which followed, the details of the mechanisms of these reactions are in many cases fairly well understood.

It is found in solution from chromium trioxide and water and a similar reaction appears to take place in tertiary butyl alcohol which is used as an oxidant. Other non-aqueous solution in which chromium trioxide has been used are glacial acetic acid and pyridine. It is probable that the chromium trioxide is complexed in the latter case. Acetone has also been used as a solvent. Since acetic acid, pyridine and water are soluble in all proportions, an interesting spectrophotometric study would be to determine the state of chromium trioxide in varying mixtures of these solvents. In water there are some additional equilibria.

The stoichiometry of chromic acid oxidation is of interest when examining its conditions of use. Thus, with ethyl
alcohol for example, the net reaction is giving a stoichiometric ratio of one mole dischromate to three moles of alcohol to eight moles of acid.

Fieser lists various conditions under which chromium trioxide is used as an oxidising agent. He considers the oxidising power of the reagent to increase with decreasing water contents of the solvent. The chromium trioxide reactions are vigorous and potentially dangerous.

Reviews of dichromate oxidation have been given by Westheimer and Waters. The best procedure seems to be to deal with chromic acid oxidations in the classes suggested by Waters, viz. alcohols, aldehydes, hydrocarbons.

If anions such as the chloride, sulphate or phosphate are added to an aqueous solution of chromium(vi), one observes a change in visible spectrum which can be correlated with the formation of a new species. The reactivity of the ion produced in this manner will be a function of the anion which is attached.

**Nature of the oxidising species:**

Complex formation between chromic acid and an anion results in a change in the dissociation constant. In general, the more electron withdrawing anions lead to larger dissociation constants. Then the order of increasing effect on the constant is $H_3PO_4 < HCl < H_2SO_4 < HClO_4 < HNO_3$. The position of nitric acid is anomalous.

Organic compounds are often not soluble in water, and therefore a mixed solvent is commonly used in effecting chromic acid oxidations. Relatively few compounds are resistant to oxida-
tion by chromic acid and the choice is fairly limited. The majority of work has employed acetic acid as the co-solvent. The monomer dimer equilibrium constant in 91% acetic acid has been determined, although it is still not clear whether monomeric chromium(vi) exist in this medium as the acid chromate ion or as the acetochromate ion \((\text{CH}_3\text{CO}_2\text{CrO}_4^{-})\).

Besides chromic acid, the two most commonly used chromium(vi) derivatives are chromyl chloride and chromyl acetate. The first is prepared by the reaction of chromium trioxide with hydrogen chloride or of potassium dichromate with sodium chloride and sulphuric acid. It is a deep red liquid, which decompose on treatment with water and which is readily soluble in unreactive organic solvents, such as carbon tetrachloride and carbon disulphide. Chromyl acetate is prepared by the addition of chromium trioxide to acetic anhydride.

The most common lower oxidation state is chromium(iii) and oxidation generally lead to this state. However, few of the reactions lead either to chromium(v) or chromium(iv) as an intermediate. These compounds may effect further oxidations and may lead to products different than those formed in the initial chromium(vi) oxidation.

Not only an chromium(iv) and (v) known as isolable species which are unstable on treatment with water, but good evidence is also available to show that they are reaction intermediates. This should not be surprising since the conversion of chromium(vi) to chromium(iii) is a three-electron reduction, whereas few oxidations involves more than a net two-electron process. The best evidence for transient chromium intermediates
come from the phenomenon of induced oxidation and many examples of such oxidation are found in the reaction of chromium(vi) with other inorganic ions.

Oxidation of saturated C-H bond:

The chromium(vi) oxidation at saturated carbon-hydrogen bonds may be conveniently divided into three classes: those in which the oxidation occurs to an aromatic ring, then in which oxidation occurs to a double bond and which involve oxidation of purely aliphatic groupings. The first class has found considerable use in the preparation of aryl carboxylic acid and aromatic aldehydes, as well as for the determination of the orientation of alkyl groups attached to the aromatic nucleus. The other two classes of oxidation have been of less interest in synthetic work because they generally lead to mixtures of compounds which are formed in low yield.

Five different reagents have been frequently used to effect oxidation of carbon-hydrogen bonds by chromium(vi). Chromic acid in water, in acetic acid or in aqueous acetic acid, dichromate ion in aqueous solution at an elevated temperature, chromyl acetate in acetic anhydride, tert-butyl chromate in a variety of solvents and chromyl chloride in an inert solvent such as carbon disulphide or carbontetrachloride.

Oxidation at a double bond:

The oxidation of alkenes may lead to several different products. Two types of mechanism are possible for allylic oxidation. In the first a hydrogen atom (or hydride ion) is removed from the alkene giving an allylic free radical or
carbonium ion), which is ultimately converted to the unsaturated ketone. In the second, oxidation at the double bond leads to a derivative of a ketol. Elimination water then leads to the unsaturated ketone. The oxidation may also lead to an epoxide, a ketol, acids or ketones derived by cleavage of double bonds, or acids or ketones having the same number of carbon atoms as the alkene via a rearrangement. As a consequence of the variety of reactions, chromic acid oxidation of alkenes is not a generally useful synthetic reaction, but is useful in some special cases such as the tetraphenyl ethylenes.

Oxidation of alcohols:

The major use of chromic acid in synthetic chemistry is in the oxidation of primary and secondary alcohols to aldehydes and ketones respectively. As a result alcohol oxidation by this reagent has received extensive investigation. Many forms of Cr(vi) have been used, chromic acid in water or aqueous acetic acid catalysed by mineral acid; chromic acid in water-acetone catalysed by mineral acid; sodium dichromate in acetic acid; chromium trioxide pyridine complex and tert-butyl chromate. Each of these has some advantages.

One of the first investigations of the chromic acid oxidation of diols was reported by Slack and Waters. They found that the oxidation of ethylene glycol led to only small amount of cleavage (1-2% formaldehyde being isolated), and that 2,3-butylen glycol gave somewhat more cleavage (20-30%). A more detailed investigation was reported by Chatterjee and Mukherjee. The effect of methyl substitution on the degree of cleavage was
confirmed and it was found that pinacol readily gave cleavage to acetone.

**Oxidation of aldehydes:**

The chromic acid oxidation of aldehydes is not particularly useful as a synthetic method since aldehydes are generally more difficult to obtain than are the corresponding carboxylic acids. However, the oxidation does proceed in a satisfactory fashion. Heptanoic acid is obtained in 70% yield from the aldehyde, and furfural is converted to furoic acid in 75% yield. Further, the aldehyde is an intermediate in more common oxidation of a primary alcohol to a carboxylic acid.

The first kinetic study of the chromic acid oxidation of aldehydes was reported by Lucchi. He studied the oxidation of a series of aromatic aldehydes in acetic acid solution using sulphuric acid as the catalyst. The reaction was first order in aldehyde and in chromium(vi). Electron withdrawing substituents were found to facilitate the reaction.

**Oxidation of ketones:**

The chromic acid oxidation of ketones generally leads to carbon-carbon bond cleavage with the formation of two carboxylic acids. Thus diethyl ketone gives propionic acid and acetic acids, and cyclohexanone gives adipic acid along with some glutaric and succinic acids. The relative rates of oxidation of series of cycloalkanones has been determined and the order of decreasing reactivity was found to be $C_6$, $C_9$, $C_8$, $C_5$, $C_7$, $C_4$. The rates of oxidation of a series of methyl alkyl ketones has also been studied and the rates of reaction were found to
increase with increasing chain length. The kinetics of the chromic acid oxidation of cyclohexanone has been studied. The rate of reaction was found to be proportional to the concentration of ketone, acid chromate ion and acid. Best et al interpreted the solvent isotope effect \( k_{D_2O}/k_{H_2O} = 4-5 \) in terms of an attack on the enol form of the ketone. This was supported by Rocek and Riehl, who have also shown that 2-chlorocyclohexanone and isobutyrophenone are oxidised via their enol form. Petit et al have done some work on the oxidation of aliphatic ketones. Bakore and others have carried out the oxidation of some aliphatic ketones. They have observed that the oxidation is being carried out by monomeric species. Increase in acetic acid proportion increases the rate of oxidation. The relative rates of oxidation and enolisation reaction run parallel. So oxidation through enol intermediate has been proposed.